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Progress Report

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Design of Tandemly Operated Fast Scan High Resolution Mass Spectrometer-Gas Chromatography

Final details have now been worked out in this laboratory for an entirely new concept in mass spectrometry - a fast electrical scan high resolution mass spectrometer whereby one can rapidly monitor gas chromatographic effluents containing one microgram or less by recording in real time or on FM magnetic tape, spectra extending over a decade in mass with a resolving power in the order of one in 10,000 or more at scan speeds of about 5 to 10 seconds. The system is devised in such a manner that the data procured is readily amenable to computer techniques. Under the circumstances the mass of all the fragments produced in a spectrum can be measured to an average accuracy of better than ten parts per million. With these accuracies in hand it was then possible for us to devise computer programs to provide elemental compositions of each fragment in the form of 'element maps'. With the exception of the input of the necessary control information, the entire processing of the recorded spectrum was performed by the analog to digital converter and the digital computer. Within the next few months we hope to optimize the analog to digital conversions making the data processing a real time function.

After exploring many different gas chromatographic column systems for use with the tandemly operated instrument it soon became apparent that the support coated capillary column devised by Dr. C. Horvath now associated with our laboratories, was ideal for the application of the combined laboratory instrument system to structural problems. (It also appears that this type of column will be eminently suited for use in a space borne instrument). Unlike the conventional liquid phase coated open tubular columns this column accepts a wide range of sample sizes without serious overloading. Moreover, sample splitting may be avoided or if necessary small sample split ratios (1 to 4-8) can be used. The carrier gas flow rates are low and the concentration of solutes in the gas phase high - providing ideal conditions for the use of enrichment devices for interfacing of the two instruments. When compared to packed columns, plate numbers exceeding 500 theoretical plates per foot are easily obtained. The columns can be readily reproduced and if necessary can be made to contain a relatively high ratio of liquid phase volume to gas volume. Under these circumstances they are excellent for the analysis of trace components.

Publications:

Fast Scan High Resolution Mass Spectrometry
1. Operating Parameters and Its Tandem Use with Gas Chromatography

W.J. McMurray, B.N. Green, and S.R. Lipsky. Anal. Chem., 38, 1194 (1966)

Enrichment Devices

A very essential part of the tandemly operated mass spectrometer - gas chromatograph instrument is the system used to interface the two instruments. Ideally, this system should be capable of selectively and dynamically removing much of the carrier gas (helium or hydrogen) from the gas chromatographic column effluent with little or no loss of the sample solute (sample enrichment) prior to its entry into the ion source of the mass spectrometer. This is necessary for the maintenance of an adequate vacuum in the mass spectrometer in order to provide good interpretable fragmentation patterns at high sensitivity. Prior to the recent developments from this laboratory, two systems were available for this purpose. The first described was the molecular separator developed by Ryhage of the Karolinska Institute, based on the jet principles outlined by E. Becker for the separation of uranium isotopes by gaseous diffusion. In our hands a model of this device procured from Ryhage was found to provide an efficiency of approximately 3-4%. For this purpose, relative efficiencies were determined in the following manner. A one microgram sample of methyl stearate was placed on a direct insertion probe and then put directly into the ion source of the mass spectrometer. The ionization current generated by the sample was then measured as a function of time. The area under the curve was taken to represent 100% efficiency. The same one microgram was then injected into the gas chromatographic column, from which it then passed into the enrichment device. At this point, depending upon its principle of operation, a variable quantity of helium as well as some sample was dynamically pumped away from the device. The enriched, remaining sample then entered the ion source. Under these conditions, the ion current generated by the sample was again measured as a function against time and compared with that observed when the sample was placed directly into the source. When Ryhage was informed of these findings he recommended certain design changes which we incorporated into our system. In our hands the efficiency then increased from 3% to 15%.

Because of these results we then explored the use of the Watson-Biemann separator which consisted of jacketed ultra fine porous glass tube with constrictions at either end. After exploring all the variables involved we found this to be a relatively simple device which when optimized provided efficiencies in the range of 12 to 15%. After assessing the situation it was decided that both devices while filling a technological gap still left much to be desired, not only for use in the laboratory but much more important, for utilization in space borne instruments. The Ryhage device contained a series of jets with orifices .002 to .004 of an inch internal diameter which were susceptible to plugging. Moreover, the pumping requirements were rather stringent - a roughing pump on the first stage, a diffusion pump on the second stage. On the other hand, pumping was much more simplified with the Watson device but because of relatively low efficiencies plus the fact that its operation depended upon a fritted glass tube which could not tolerate the rigors of a space vehicle launch it was decided to explore other means of accomplishing a very efficient enrichment system that would be satisfactory for space borne operations.

After a years work we are delighted to now report that we have accomplished our goals in this sphere. In essence we now have a device which can readily withstand blast off and prolonged space flight. It can be made to weigh no more than 10 to 15 grams. It has very simple pumping requirements and tests thus far have shown that it provides incredibly good efficiencies - in the order of 60 to 80%, depending upon the temperature of operation.

Principle of Operation of the New Device

It has long been known that certain plastic films exhibit varying degrees of permeability to gases. Since our requirements necessitated the use of relatively high temperatures for the satisfactory operations of the tandemly operated gas chromatograph-mass spectrometer (200-275° C) only those membranes which could tolerate these temperatures under vacuum were examined. Two appeared suitable for this purpose - Teflon FEP, a copolymer of tetrafluoroethylene, and hexafluoropropylene and Silicone rubber and its derivatives. In general it was found that gas permeation through a membrane is a complex transport process caused by a partial pressure differential between the two sides of the membrane. The gas dissolves in the membrane at its high pressure side, passes through the membrane by activated diffusion and evaporates from the opposite side. The diffusional step is rate determining and under steady state conditions, obeys Fick's law

$$q = -DA \frac{dc}{dx}$$

where q is the amount of gas diffusing through the membrane of area A per unit time, D is the diffusion constant and dc/dx is the concentration gradient across the membrane. If D is independent of concentration the above equation can be integrated over T (the thickness of the membrane) to yield

$$q = DA \frac{(C_H - C_L)}{T}$$

where C_H and C_L are the concentration of gas near the high - and low pressure sides respectively. If the solubility of the gas in the membrane is low (as is the case for the higher molecular weight solutes dissolved in the low molecular weight carrier gas i.e. helium or hydrogen as the effluent emerges from the gas chromatographic column) it may obey Henry's law

$$C = S_p$$

where c is the concentration of the gas dissolved near the interfaces of the membrane when its partial pressure is p and S is the solubility constant. Substituting

$$q = DS\,\frac{(p^H - p^L)}{T} = p\,\frac{A(p^H - p^L)}{T}$$

one obtains the permeability rate P. P was found to be dependent upon the nature of the carrier gas and the membrane and the temperature at which the membrane was maintaned. Permeability was found to increase exponentially with temperature. Operation at 250°C was found to provide maximum diffusion of helium through the membrane with minimum loss of solute sample by means of solubilization across the membrane.

The teflon membrane system we have devised was found to possess many distinct advantages for our laboratory and space applications.

a) It is now exceedingly simple to construct and use

b) The pumping requirements for space use are minimal in comparison to other enrichment devices

c) It can be made into an exceedingly rugged and light weight system (~10-15 grams)

d) It has a high absolute permeability to helium

e) It has a high selectivity for helium (a high permeability to helium relative to other components that may be found in the gas chromatographic effluents i.e. organic compounds with molecular weights extending from 5 to 300+).

f) It has great physical stability and chemical inertness.

g) It provides a continuous uniform surface free of pin holes or other defects.

An example of the excellent results obtained with this enrichment device may be seen from an inspection of the enclosed chromatogram obtained from our gas chromatograph-high resolution mass spectrometer tandemly operated instrument utilizing a teflon membrane interface.

Conditions:

Slits: set for resolution of 1 in 12:000

Trap current: 500 microamperes

Attenuation: X50

Temperature of teflon membrane: 252° C

Temperature of chromatographic column: 175° C

Column: 3 feet x 1/8" i.d. containing 12% ethylene glycol succinate coated on 80-100 mesh Chromosorb W

Helium Pressure at inlet: 10 psi

Sample: 7.5 micrograms injected onto gas chromatographic column

a) solvent

b) methyl laurate (C-12) 1.0 microgram

c) methyl myristate (C-14) 1.5 microgram

d) methyl palmitate (C-16) 2.0 microgram

e) methyl stearate (-C-18) 3.0 microgram

Detector:

Total Ion Beam Current Monitor, Mass Spectrometer

Publications:

a) Fast Scan High Resolution Mass Spectrometry

2. The Utilization of Gas Permeation Through Membranes for its Tandem Use with Gas Chromatography.

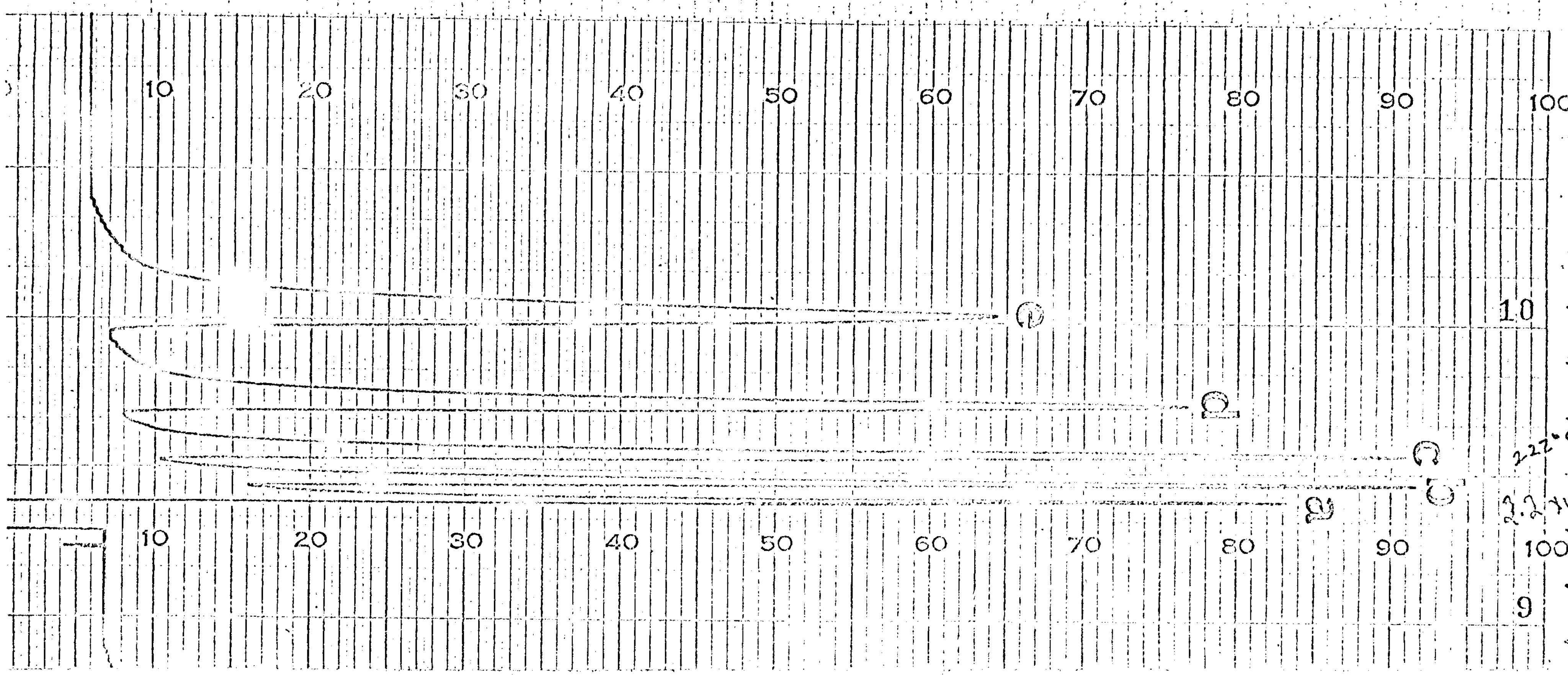
S.R. Lipsky, C. Horvath, and W.J. McMurray

Accepted for presentation and publication in the Proceedings of the Sixth International Symposium on Gas Chromatography and Associated Techniques, September 1966.

b) The Utilization of a System Employing the Selective Permeation of Helium Through a Unique Membrane of Teflon as an Interface for a Gas Chromatograph and a Mass Spectrometer

S.R. Lipsky, C. Horvath and W.J. McMurray. Accepted for publication, Analytical Chemistry, October 1966.

The successful completion in this laboratory of all major aspects of the development of a fast electrical scan high resolution mass spectrometer-gas chromatograph tandemly operated instrument as well as an exceedingly efficient enrichment device for the interfacing of both devices now paves the way for an extensive scientific backup program to be carried out in collaboration with our colleagues at the Jet Propulsion Laboratory, California Institute of Technology. This will involve the utilization of this overall system in a study of the chemical composition of a wide range of materials contained in soil and rock samples from significantly different environments. In this regard,



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computer programs also developed in this laboratory have been found to not only facilitate the acquisition of mass spectral data but also the interpretation of mass spectra. Thus the rapid acquisition as well as the uniform handling of data should permit the smooth exchange of large amounts of important information between collaborating laboratories.

During the past six months Dr. Lipsky has had the opportunity to have extensive discussions with Dr. Alfred Nier, Professor and Chairman of the Department of Physics at the University of Minnesota concerning the 'breadboarding' of a miniature, light weight gas chromatograph-mass spectrometer which would serve as a prototype for the development of a space borne instrument to be used for the analysis of planetary atmospheres as well as the detection and identification of organic compounds which may be found on planetary surfaces. In an attempt to facilitate the program as well as save time and large sums of money, Dr. Lipsky and Dr. Nier decided upon an informal collaborative effort to examine all the parameters necessary for the evolution of the 'breadboard' device by the end of 1966 or early 1967. Accordingly, Dr. Nier is now in the process of constructing a small double focusing mass spectrometer for this specific purpose. When this device is near completion Dr. Lipsky will visit with Dr. Nier in order to go over the details of the instrumentation and to undertake the interfacing of the light weight mass spectrometer with the gas chromatograph. As it now stands Dr. Nier will then place the instrument in Dr. Lipsky's laboratory for 30 to 90 days for intensive evaluation of the operational features of the tandemly used instruments. Following this, a full reassessment will be made by both laboratories and if necessary, appropriate changes will be instituted. When a very satisfactory 'breadboard' emerges, our colleagues at JPL will undertake a study of this system and compare it with other prototype units. A device will then be constructed by JPL for use in the planetary exploration program. All interested parties will be kept fully informed of the progress of these undertakings at all times.